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Test Plan for Composite Hydrogen Getter Materials

Prepared under Technical Task Plan Number SR1-9-MW-45
Principal Investigator: Ronald R. Livingston

Strategic Materials Technology Department
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I. Contents:

II. List of Abbreviations and Acronyms

CAO	Carlsbad Area Office
CH-TRU	contact-handled transuranic waste
CMH	composite metal hydride
DEB	1,4-bis(phenylethynyl)benzene
DOE	Department of Energy
ICV	inner containment vessel
INEEL	Idaho National Environmental Engineering Laboratory
LANA1	lanthanum nickel aluminum ($LaNi_{4.0}Al_{1.0}$)
LANL	Los Alamos National Laboratory
MWFA	Mixed Waste Focus Area
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PVT	pressure-volume-temperature
QA/QC	quality assurance/quality control
RFETS	Rocky Flats Environmental Technology Site
SARP	safety analysis report for packaging
SGMH	sol-gel metal hydride
SOW	statement of work
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TCE	trichloroethylene
TRUPACT-II	Transuranic Package Transporter-II
TTP	technical task plan
VOCs	volatile organic compounds

III. Summary

The intent of this test plan is to provide details of the Savannah River Technology Center (SRTC) effort to evaluate composite getter materials for eventual use in expanding the wattage limits for transportation of contact-handled transuranic waste (CH-TRU). This effort is funded by the Mixed Waste Focus Area (MWFA) under Technical Task Plan (TTP) SR-1-9-MW-45 and is the result of a competitive process initiated by a MWFA request for proposals.[1] In response to this request, SRTC presented data on several composite getter materials that demonstrated good potential for application in transportation of transuranic wastes.[2] The tests outlined in the SRTC proposal for composite getter materials should demonstrate compliance with functional requirements provided by the MWFA in a Statement of Work (SOW) which accompanied the request for proposals. Completion of Phase 1 testing, as defined in the TTP, should provide sufficient data to determine if composite getters should progress to Phases 2 and 3. These test results will provide support for future safety reviews as part of the Transuranic Package Transporter-II (TRUPACT-II) certification process to utilize getter technology.

This test plan provides details of the test descriptions, test objectives, required measurements, data quality objectives, data analysis, and schedule information relevant to Phase 1 of the TTP. The results of these tests are expected to help identify any potential weaknesses in the use of composite getter for transportation of CH-TRU wastes. Where a potential weakness is identified, this will be addressed as part of Phase 2 of the proposed effort. It is also important to recognize that these tests are focused on the individual composite getter materials and not the engineered system that would eventually be used in a TRUPACT-II. However, these test results will be very helpful in establishing the requirements for the design of a TRUPACT-II getter system that is included as part of the proposed Phase 3 effort.

IV. Background

<u>Target Problem</u>

Interaction of radiation from TRU elements with the waste matrix being transported in the TRUPACT-II results in decomposition of the waste and production of non-radioactive gaseous by-products. Additional gases and vapors may be present in the sealed TRU waste containers from other sources, such as volatilization of waste content and thermal or biological degradation of waste components. The headspace of TRU wasted drums has been shown to include gases and vapors such as hydrogen, oxygen, carbon dioxide, carbon monoxide, methane, trichloroethylene (TCE), hydrogen chloride, and acetone.[3, 4, 5, 6] The accumulation of hydrogen within the individual waste packages and drums, as well as within the sealed TRUPACT-II inner containment vessel (ICV), presents a safety hazard. The Safety Analysis Report for the TRUPACT-II Shipping Package (TRUPACT-II SARP)[7] limits the hydrogen concentration to less than 5% by volume to avoid forming flammable gas mixtures.

A 40-Watt (40-W) limit has been placed on the overall radioactive decay energy of the TRUPACT-II contents, based on the package's ability to dissipate the decay heat. However, the character of TRU waste matrices and the energy of some radioactive contaminants prevent the container from being loaded to the full 40-W limit because the amount of hydrogen produced could result in flammable gas mixtures. The amount of hydrogen generated is a function of both the waste type and the decay energy; therefore, operating limits for allowable radioactive decay energy in the TRUPACT-II have been established for different waste types. For wastes contaminated with Pu-238, which decays at about 0.5 W/g, the total TRUPACT-II loading may be limited to only 3 W (6 g Pu-238).

The current SRS waste inventory includes about 7000 drums of Pu-238-contaminated waste, with more than half of these containing greater than 6 g of Pu-238.[8] Needs for technologies to prevent hydrogen accumulation in the TRUPACT-II exist at other sites within the DOE that have high-wattage level wastes. The needs include Pu-238 waste at LANL, and Am-Cm wastes at Hanford, INEEL, ORNL, and RFETS. Due to current decay energy operating limits, drums of this type of waste cannot be shipped without repackaging to decrease the overall decay energy per drum. This will ultimately result in more shipments and higher transportation costs per waste drum.

To address this problem, a call was issued for the development of technologies to mitigate hydrogen accumulation in the TRUPACT-II and evaluation of alternative options for TRU packaging.[1] The Department of Energy's (DOE's) MWFA and Carlsbad Area Office (CAO) are working to reduce the costs of transporting TRU waste by developing technologies that will take advantage of the full 40-W decay energy limit for the TRUPACT-II.[9] If successful, the need for repackaging will be minimized and the number of waste shipments reduced.

Two complementary approaches to increasing the TRUPACT-II wattage limits are being taken. The first approach is to package the waste in a way that minimizes the number of confinement layers and allows hydrogen to diffuse out of individual packages and drums and into the ICV of the TRUPACT-II. This approach will allow waste limits to be calculated based on hydrogen concentration in the minimum void volume of the ICV (2450 L for a 14-drum payload) rather than in the small internal volumes of individual 4-L packages.[7] The second approach is to remove hydrogen from the ICV by reaction with or absorption by another material. This removal step is referred to as "gettering" hydrogen. Use of an appropriate getter material to remove hydrogen from the ICV as it is generated should enable the hydrogen concentration to be kept below the 5% lower flammability limit.

Technology Description

The term "metal hydride" is commonly used to refer to a metal or metal alloy that reacts reversibly with hydrogen, whether or not it is in the hydride form. Metal hydrides have been studied and used for purposes of hydrogen separation and storage for some time.[10]

In general, metal hydrides absorb hydrogen at lower temperatures and desorb hydrogen at higher temperatures, although the functional temperature range varies widely for different metal hydrides. The fact that the reaction is reversible suggests metal hydrides used as hydrogen getters in the TRUPACT-II could be recycled and reused, resulting in significant savings in the costs associated with transporting TRU waste.

When metal hydrides are exposed to certain gases called poisons, the absorption of hydrogen is reduced or prevented altogether. Also, repeated absorption and desorption of hydrogen causes metal hydride particles to break down (decrepitate) into micron-size fines, which can lead to a number of engineering concerns. Both of these problems have been largely eliminated by the development of a composite getter material called sol-gel metal hydride (SGMH).[11] [Note: In general, the term composite metal hydride (CMH) will be used to indicate both sol-gel metal hydride as well as other composite metal hydrides developed within SRTC. The specific formulations of these materials are not disclosed to protect future patent rights.]

SGMH consists of particles of metal hydride (typically less than 50 μm) encapsulated in a porous silica-gel matrix formed by a sol-gel process. The resulting product is typically crushed or ground into particles 1-5 mm in size. The pore sizes of the SGMH particles are large enough to permit hydrogen to enter the matrix, but small enough to inhibit the passage of larger molecules such as oxygen and carbon monoxide that could poison the metal surface. Tests on SGMH indicate the encapsulated metal absorbs hydrogen reversibly just as the unencapsulated sample does. Also, after 100 absorption/desorption cycles the metal hydride particles are retained within the silica matrix and there is no further breakdown of the SGMH particles.[11]

Prior Year Progress

CMH samples were prepared by encapsulating metal hydride particles into a porous silica matrix or other matrix materials to create a composite form. These composite getters have been shown to protect the active metal surface from small poison molecules such as oxygen (air) and carbon monoxide.[11] Thus, the protective mechanism is expected to protect from larger poison molecules as well. Hydrogen absorption rates in air for CMH are from 10 to 100 times greater than those observed for the unprotected metal, and the composite getters have been demonstrated to absorb hydrogen from air across the required temperature range.

Several metals have been evaluated for suitability, and two have shown the most promise—$NdCo_3$ and $LaNi_{4.0}Al_{1.0}$ (LANA1). $NdCo_3$ composites are likely to become the preferred alternative [Note: The decision to switch from ZrCo to $NdCo_3$ was made in 6/2000.] based on its greater hydrogen capacity and good kinetics over the required temperature range. $NdCo_3$ also shows smaller reduction of capacity at 160°F than composites produced using LANA1. However, LANA1 composites will continue to be considered our primary getter material, based on material costs and ease of use, until the potential improvements offered by $NdCo_3$ can be further demonstrated. The flexibility and demonstrated use of these composite materials are anticipated to provide the poison protection essential for use of getters to remove hydrogen in packaging and transportation applications.

V. Composite Getter Testing and Evaluation

Test Objectives

The objectives of this test plan are to demonstrate the capability of composite getter materials to function under non-ideal conditions anticipated as normal conditions of transport for the TRUPACT-II. These conditions (i.e., temperature, gas composition, pressure, etc.) have been defined by the MWFA and CAO in the Statement of Work issued as part of the request for proposals for the Hydrogen Gas Getters Evaluation Program.

One goal of this test plan is to establish that the necessary degree of project planning has been completed in order to initiate evaluation of composite getter materials for potential use in the TRUPACT-II. There may continue to be discussion of desired test conditions and additional ideas generated to improve the proposed test scheme after issue of this document. These improvements will be implemented at the discretion of the principal investigator, where changes do not impact the completion of TTP milestones. These milestones are best defined as part of the TTP task descriptions provided in subtasks 2-7 described in the following section.

TTP Subtasks

Tasks for FY2000 will involve Phase 1 activities (“Hydrogen Getter Evaluation”) and, as appropriate, the initial stages of Phase 2 (“Getter Material Enhancement and Evaluation”). The TTP for FY2000 includes nine major subtasks—seven are related to Phase 1 activities and two are related to Phase 2 activities. All TTP activities—with the exception of the Headquarters Milestone—are to be delayed two months due to funding delays at the Savannah River Site (SRS). LANA1 SGMH will be tested as part of subtasks 2 through 6 defined below. If scale-up preparation is successful, two additional materials, LANA 1 CMH and $NdCo_3$ CMH, will also be evaluated.

Subtask 1: Develop Test Plan (*Note: This document is the subject of this subtask*.)

A test plan will be developed that discusses experiments to be conducted as part of Phase 1 activities. The major areas of study for FY2000 are listed below as subtasks 2-7. The test plan must be reviewed and approved by the MWFA.

Subtask 2: Evaluate Potential Poisons

Many potential poisons can be present in the TRUPACT-II.[3, 4, 5, 6] The poisons are grouped into three categories: flammable volatile organic compounds (VOCs), nonflammable VOCs, and inorganics. A few poisons from each category will be selected to determine their effect on the CMH samples after prolonged exposure. Samples will also be tested that have experienced prolonged exposure to air.

Evaluating potential poisons is the most important part of getter testing and ultimately may have to be expanded to address any Nuclear Regulatory Commission (NRC) concerns. Tests planned for Phase 1 will screen CMH to determine if representative poisons have a detrimental effect on getter performance. A wider range of poison tests is planned for Phase 2 that includes more potential poisons, longer exposures, and repeated temperature cycles. Poisons tested in Phase 2 should be selected to help certify the getter material(s) for selected waste streams.

Subtask 3: Evaluate Operating Temperature and Pressure Range

The hydrogen getter must be capable of absorbing hydrogen over a range of temperatures from –20^{o}F to 160^{o}F. Tests will be conducted to measure the hydrogen capacity and equilibrium hydrogen pressure at 160^{o}F, and kinetics at three temperatures: –20^{o}F, ambient temperature (approx. 70^{o}F), and 160^{o}F. The regulations for the TRUPACT-II also state that operating conditions include both atmospheric pressure and 50 psig. Consequently, the getter will be tested at 0, 15, and 50 psig.

Subtask 4: Absorption Reaction Reversibility

The getter must be capable of absorbing hydrogen below a concentration of 5% in air and maintaining it below that level. With CMH samples, the potential for desorption occurs when a loaded sample is subjected to increasing temperatures. Tests will demonstrate that CMH will not release hydrogen in excess of the 5% hydrogen concentration limit when loaded to its rated capacity at ambient temperature, then heated to 160^{o}F (while accounting for pressure changes due to temperature).

Subtask 5: Getter Operational Life

The getter must be capable of absorbing hydrogen at the identified rates and for the anticipated storage and shipping times. Because the CMH will be used in the ICV, an operational life of 60 days is required. The test will be scaled such that there is sufficient CMH sample to function for 60 days. However, in the interest of time, the experiment will be conducted so the absorption rate of hydrogen can be measured as a function of remaining getter capacity (operational life is a function of available getter capacity).

Subtask 6: Demonstrate the Absence of Free Liquids

Experiments will be conducted to confirm that the free liquid requirement is met. One set of tests will focus on quantifying the amount of moisture that can be absorbed by the candidate matrices by exposing them to water vapor for prolonged periods of time and measuring their weight gain. In a separate test the ratio of gas space to CMH sample will be scaled to that anticipated for deployment in the TRUPACT-II. Next, the sample will recombine hydrogen and oxygen in air until the overall pressure change indicates recombination is complete. Visual observations will be used to determine if liquid water is present. More detailed examination of this phenomenon should be completed as part of Phase 2 testing if necessary.

Subtask 7: Phase 1 Summary Report

Data and findings from Phase 1 efforts will be compiled into a summary report that will be used to update the MWFA on technical progress. The report will emphasize the technology's strengths as well as areas where development may still be necessary. It is anticipated that the report will provide the basis for determining whether to progress with Phase 2 activities.

Subtask 8: Optimize CMH Pore Size

Prior studies, particularly with sol-gels, show that pore sizes can be achieved that will improve poison exclusion. Two candidate CMH materials are available for testing. One candidate, based on sol-gel technology, exhibits a closing of its pores when heated. The second candidate material undergoes an opening of its pores when heated. Current CMH configurations are not optimized for poison exclusion. However, experimental data show that the CMH matrix is protecting the majority of the absorption capacity from poisoning by air.

Subtask 9: Optimize CMH Getter-Matrix Ratios

Current CMH formulations have not yet been optimized for matrix material composition or getter-to-matrix ratios. It is anticipated that CMH performance can be improved by variations in the CMH formulations, particularly by altering the getter-to-matrix ratios. Improvements will be tested using a series of tests aimed at determining absorption capacity and kinetics in air as a function of remaining absorption capacity.

<u>Hydrogen Absorption Test Method</u>

Composite getter material performance will be characterized using measurements of hydrogen gas absorption. Using this data, the effects of each test condition on the getter's absorption rate and hydrogen capacity can be measured. Absorption rate and capacity are the primary indicators that will be used to describe getter function and determine the best candidate for use in Phase 2 studies. The process of obtaining these measurements is automated and the tests are scaled for conditions anticipated in the TRUPACT-II.

Figure 1 is a schematic for one of the sections in a gas manifold used in these experiments. This arrangement simplifies the addition of an accurately known amount of gas to the sample. Typically, 0.5 to 2 grams of composite getter is introduced into the sample bed, which is subsequently attached to the gas manifold. In the case of the metal only, activation is accomplished by heating the sample to between 300 and 400°F under vacuum for 1 to 2 hours and then saturating with hydrogen. In the case of composite samples, the activation step is preceded by a period of drying the sample under vacuum while gradually heating to the activation temperature. Hydrogen is subsequently desorbed from the sample by heating under vacuum to sufficient temperature to release the hydrogen (300 to 400°F for LANA1 and 570 to 750°F for ZrCo). The sample is now ready for testing.

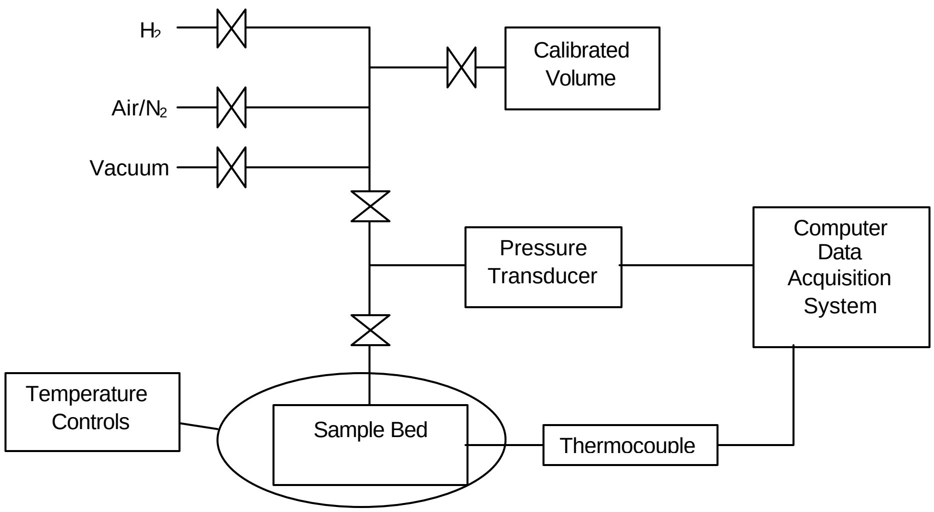


Figure 1. Schematic of hydrogen getter test apparatus.

Testing getter materials involves several steps including sample activation, exposure to test conditions, measurement of hydrogen absorption at low partial pressures and measurement of system capacity. Following activation of a composite getter sample, where required, typical absorption tests consist of the following steps to measure getter performance:

(1) the absorption rates of hydrogen (< 5%) in nitrogen and an equivalent amount of hydrogen in vacuum (i.e., no other gases present) are determined;

(2) after activation or reconditioning, an excess of hydrogen is added to the sample to determine the maximum (ideal) hydrogen capacity [Note: This capacity measurement does not take into account the amount of hydrogen potentially removed by recombination reactions to form water.];

(3) the sample is heated under vacuum to desorb hydrogen and cooled to room temperature;

(4) the sample is removed from the test apparatus and exposed to a fixed volume of air or potential poisons for a selected time period;

(5) the sample is returned to the test apparatus and the hydrogen absorption rates in vacuum and in nitrogen are re-measured to determine the effects of test conditions; and

(6) the absorption rate of hydrogen (< 5%) from air is measured.

In some instances, the sample bed is temperature-controlled at elevated temperature (~ 160°F) or reduced temperature (~ -20°F) to test the impact of thermal conditions on sample performance. It is possible to clearly demonstrate a material's capability to protect the getter from gaseous poisons because an activated metal exposed to poisons will exhibit decreased hydrogen absorption rate and capacity to the point of deactivation. This has been shown using hydrogen in air where oxygen is a poison. Exposure of CMH samples to air over extended periods of time (about two months) show that the composite material can retain most of its hydrogen absorption capacity and sufficient absorption rate.

Test Design

The Statement of Work requires tests of the following parameters:

1. Potential Poisons
2. Compatibility
3. Operating Temperature Range
4. Pressure
5. Reversibility
6. Operational Life
7. Free Liquids
8. Temperature Effect
9. Passive Systems
10. Radiation Effects

This test plan provides for an evaluation of these parameters as independent variables but not in combination. The consequences of combined effects (e.g. exposure to potential poisons at elevated temperature) are not tested and may be evaluated as part of data analysis and review. Issues identified as part of data review can be addressed as part of the Phase 2 development and expanded testing.

The criteria used to evaluate all getter materials performance are the hydrogen capacity and absorption rate. The impact of selected test conditions on capacity and rate will be determined for each composite getter material being evaluated. The response of various composite getter materials to each test condition will be used to document getter function. These measurements are initiated by placing the getter material in a fixed volume container and adding hydrogen gas to provide the desired hydrogen concentration at a known pressure and temperature. The resulting pressure drop with time is used to calculate the getter's hydrogen absorption rate. The useful getter capacity is determined by adding additional hydrogen gas until the getter can no longer maintain an adequate rate or maintain hydrogen concentration below 5%.

Rate and capacity measurements will be made across the specified range of test conditions required by the SOW. In some cases, only the extreme conditions will be evaluated for impact on getter functions (i.e., poison concentration), and for other parameters, the getter will be tested at minimum, midpoint and maximum values (i.e., temperature and pressure). Initial measurements will be made in nitrogen environments to allow quantitative evaluation of the effects of atmospheric oxygen and moisture on getter performance. Both oxygen and moisture are included in the test matrix to allow quantification of composite getter improvements during Phase 2. The tests planned to evaluate each of the SOW parameters are described in the following section on a test program for getter evaluation.

Test Program

Evaluating Potential Poisons – Many potential poisons can be present in the TRUPACT-II.[3,4,5,6] The poisons are grouped into three categories: flammable VOCs, nonflammable VOCs, and inorganics. A few poisons from each category will be selected to determine their effect on the CMH samples after prolonged exposure. The representative poisons selected are as follows:

Flammable VOCs: acetone, methanol, and toluene
Nonflammable VOCs: chloroform and tetrachloroethylene
Inorganics: carbon monoxide, hydrogen chloride, and water vapor

At this stage of the program, the poisons will be evaluated individually. In Phase 1, based on the SOW expectation of a 3-month evaluation, there is insufficient time using our current facilities and funds to perform multiple 60-day experiments. The test will use a gas-to-sample ratio that is twice what is expected in the TRUPACT-II. The CMH sample will be loaded into the test vessel and exposed to 1000 ppm of the poison (2X the allowable poison limit for VOCs) in air for seven days; this will demonstrate potential chronic effects from the selected poisons. Gas samples will be analyzed before and after sample exposure to measure poison uptake. Following exposure, the CMH sample will undergo the standard tests described above.

Samples will also be tested that have experienced prolonged exposure to air. Samples will be activated from the initial batch of CMH and be stored in ambient conditions. The samples will be periodically tested for hydrogen absorption characteristics using the standard test. The baseline case for evaluating the impact of poisons will be hydrogen absorption rate from nitrogen gas before the sample is exposed to potential poisons.

Evaluating potential poisons is the most important part of getter testing and ultimately may have to be expanded to address any NRC concerns. Tests planned for Phase 1 will screen CMH to determine if representative poisons have a detrimental effect on getter performance. A wider range of poison tests is planned for Phase 2, which includes more potential poisons, longer exposures, and repeated temperature cycles. As necessary, the Phase 2 evaluation will determine threshold poison concentrations that affect getter performance.

Compatibility Testing – Compatibility of the getter must be ensured with respect to the chemical contents of the payload and the materials of construction of the TRUPACT-II. CMH getters are made of stable, inorganic materials similar to those listed in Tables A-2 through A-6 of the Statement of Work. Therefore, compatibility problems are not expected. However, to meet the project requirement, the following experiments will be conducted.

(A) Samples of CMH will be mixed with chemicals from the SOW list that have some reaction potential: nitric acid (pH 2), sodium hydroxide (pH 12.5), oil, and a solid organic acid. These mixed substances will be placed in an instrumented bomb calorimeter and heated to 160ºF. Temperature and pressure will be monitored so that a reaction can be discerned. [Note: This activity is not one of the stated project Milestones, and its completion during Phase 1 is dependent on equipment availability.]

(B) A second set of tests will evaluate the pyrophoric nature of CMH samples that have been loaded with hydrogen. According to the definition for pyrophoric material in the Code of Federal Regulations,[12] the CMHs produced at SRTC are not pyrophoric because CMH does not ignite upon exposure to air.

For the Phase 1 evaluation, CMH samples that are loaded with the full amount of hydrogen expected will be exposed to air and monitored for temperature rise as an indicator of combustion. If required, additional tests to evaluate the potential for pyrophoric behavior will be conducted as part of Phase 2.

Operating Temperature Range – The hydrogen getter must be capable of absorbing hydrogen over a range of temperatures from –20^{o}F to 160^{o}F. Tests will be conducted to measure the hydrogen capacity and equilibrium hydrogen pressure at 160^{o}F, and kinetics at three temperatures: –20^{o}F, ambient temperature (approx. 70^{o}F), and 160^{o}F.The experiments will be conducted using the standard test method described above.

Pressure – The regulations for the TRUPACT-II state that operating conditions include both atmospheric pressure and 50 psig. Consequently, the getter will be tested at 0, 15, and 50 psig using the standard test method.

Reversibility – The getter must be capable of absorbing hydrogen below a concentration of 5% in air and maintaining it below that level. With CMH samples, the potential for desorption occurs when a loaded sample is subjected to increasing temperatures. Tests will demonstrate that CMH will not release hydrogen in excess of the 5% hydrogen concentration limit when loaded to its rated capacity at ambient temperature, then heated to 160^{o}F (while accounting for pressure changes due to temperature).

Getter Operational Life – The getter must be capable of absorbing hydrogen at the identified rates and for the anticipated storage and shipping times. Because the CMH will be used in the ICV, an operational life of 60 days is required. The test will be scaled such that there is sufficient CMH sample to function for 60 days. However, in the interest of time, the experiment will be scaled in such a way that the absorption rate of hydrogen can be measured as a function of remaining getter capacity (operational life is a function of available getter capacity).

In order to demonstrate the kinetics of hydrogen absorption in air as a function of unused capacity, testing will simulate long-term exposure to hydrogen in air through the following sequence:

1. activate the CMH sample,
2. determine the capacity of the sample,
3. desorb the hydrogen from the sample,
4. introduce enough hydrogen into the test vessel to consume 5% of the capacity,
5. expose the getter to a low concentration (approx. 5% hydrogen in nitrogen) and measure the absorption kinetics, and
6. repeat Steps 4 and 5 at 50% and 90% of CMH capacity from Step 2. The data from this test can then be used to calculate the amount of getter that must be deployed in the TRUPACT-II.

Free Liquids – The requirement relates to determining the free liquid generation potential of the getter process. Test data indicate that the sol-gel matrix is capable of absorbing 10-15 weight percent moisture from the atmosphere. Calculations based on the total conversion of oxygen in the TRUPACT-II to water vapor indicate that complete water absorption would only require 1.5 wt. % water (by recombination of H_2 generated) to be absorbed by the matrix. Consequently, formation of free liquids is not anticipated. For waste streams that generate oxygen gas during storage and transportation (e.g., nitrate sludges), the calculation of water generated is dependent on the rate of oxygen production.

Two additional experiments will be conducted to further confirm that the free liquid requirement is met. One set of tests will focus on quantifying the amount of moisture that can be absorbed by the candidate matrices by exposing them to water vapor for prolonged periods of time and measuring their weight gain. In a separate test the ratio of gas space to CMH sample will be scaled to that anticipated for deployment in the TRUPACT-II. Next, the sample will recombine hydrogen and oxygen in air until the overall pressure change indicates recombination is complete. Visual observations will be used to determine if liquid water is present. More detailed examination of this phenomenon should be completed as part of Phase 2 testing if necessary.

Temperature Effect from Getter – This requirement involves determining the heat of reaction (in Watts) associated with the reaction of hydrogen with the getter. No experimental work is necessary. The heat of reaction for the metal hydride has already been measured at 30 kcal/mol H_2. Under worst-case conditions, assuming only recombination, the heat of reaction is 68 kcal/mol H_2. Using the stated hydrogen generation rate for the ICV of 1.2×10^{-5} mole H_2/sec, heat generation is 1.5 Watts for the hydriding reaction (ideal case) and 3.4 Watts for the recombination reaction (worst-case).

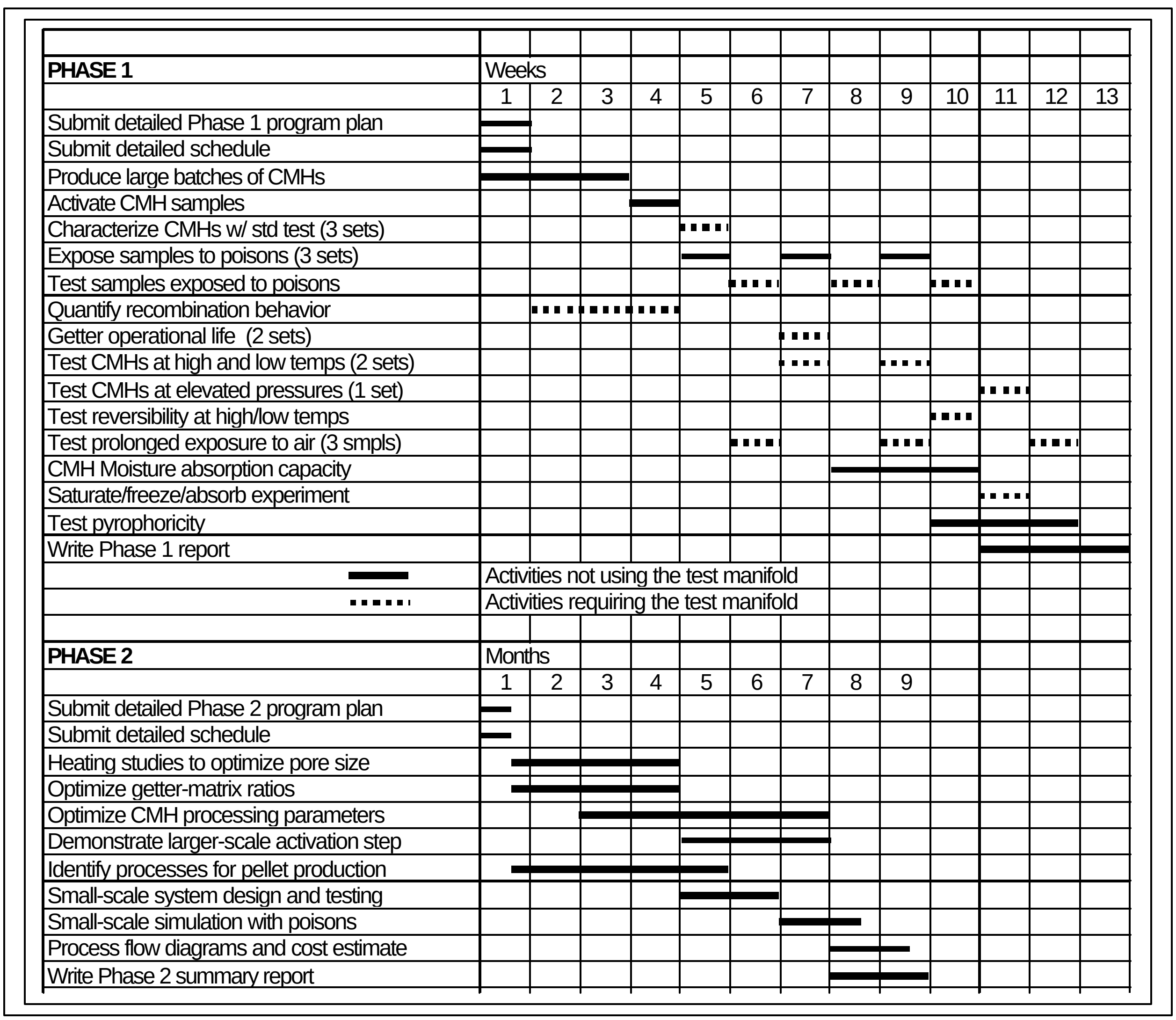
Current experimental data implies that the actual performance of the CMH potentially involves both the hydriding and recombination reactions.

Radiation Effects – Radiation effects need not be tested because the CMH will be placed inside the ICV. SRTC has the capabilities to provide these measurements if desired. However, little impact is anticipated since the individual CMH components have shown excellent resistance to radiation exposure as part of other programs.

Passive Getter System – No testing is necessary because CMH is a passive system.

Test Sequence

Scheduling for test activities is shown below as presented in the initial SRTC proposal for evaluation of composite getter materials. The current estimate of these activities has changed slightly as a result of resource limitations. However, the milestones presented in the TTP should be met once the requested two-month slip in activities due to a SRS delay in project funding is taken into account. [Note: This suggests that Phase 2 activities will be delayed until FY01.]



VI. Data Quality Requirements

The data collected as part of these tests must have sufficient pedigree to establish the veracity of each test. The key measurements for this test plan include pressure-volume-temperature (PVT) measurements and gas composition measurements. The PVT measurements are sufficiently accurate using vendor supplied calibrations and test services that no special effort will be placed on additional equipment evaluation or QA/QC documentation. The gas composition measurements will be provided by gas chromatography with the appropriate detector for the desired measurement (e.g., mass spectrometer or thermal conductivity detector). The routine QA associated with the use of these instrumental methods of analysis is sufficient for the intended purpose. Replicate measurements will be made on selected samples to confirm measurement precision. The PVT data are captured electronically and handled to assure appropriate data security.

All testing will be documented in laboratory notebooks. These tests will be subjected to regular peer review by the project team members and by selected senior laboratory and plant, technical support personnel. Data analysis will be performed concurrent with laboratory testing. Tables describing testing results will be updated on a regular basis to support getter material evaluation.

Test Apparatus

The primary piece of test apparatus is the gas manifold illustrated previously in Figure 1. This manifold is constructed using stainless steel components with gas-tight Cajon™ fittings and welded tubing. The pressure transducers are high accuracy Baratrons manufactured by MKS, and the valves used in this system contain metal bellows to assure minimum leak rates. Regular leak checks are performed as part of the system operation to assure that the measured hydrogen absorption rates are not impacted by gas leaks.

Test apparatus to be used for exposure of the composite materials to poison gases and vapors were constructed by the SRTC glass shop. These rely on the equilibrium vapor pressure of the selected poison over the pure liquid to provide the poison vapor for each test. The poison tests will be conducted in sealed chambers with an injection port to allow introduction of the poison vapor and subsequent sampling for lab analysis.

Lab Analysis

Gas samples will be collected in gas-tight syringes and submitted to the SRTC analytical section for routine gas chromatographic analysis. The measurements required to support this effort are not anticipated to require any special attention with regard to normal instrument detection limits. Scanning electron microscopy, particle size analysis, and surface area measurements may also be used to support the evaluation of composite getter materials.

Getter Composition

The preparation of each composite getter material will be controlled to ensure reproducible composition. Getter composition will be estimated using standard measurements of mass, volume, material purity, and time. The sol-gel composition is provided by previously disclosed SRTC efforts covered by US patent. Other composite getter compositions remain proprietary as the potential for patent coverage is considered. Each composite is manufactured from low–cost relatively abundant components that would not impose an economic hardship on the eventual preparation and use of these materials. Each composite has unique features that are anticipated to help prevent getter poisoning, absorb excess moisture generated by recombination of hydrogen and oxygen, and provide additional features that allow easier engineering implementation of the getter in the TRUPACT-II.

VII. Data Reduction and Analysis

The following sections are excerpts from reference 2 and are intended to illustrate the type of data that will be generated as a result of this evaluation. Data reduction is accomplished using primarily spreadsheets containing data from the computer controlled data acquisition system attached to the gas manifold pressure transducers and sample bed thermocouples. Graphs of sample data demonstrating hydrogen absorption rate and tables of compiled results for multiple samples are used extensively as part of data analysis to support comparison of test conditions.

Sample Data and Calculations[2]

The absorption rates of hydrogen from air for LANA1 and LANA1 SGMH containing equal amounts of metal are shown in Figure 5. Following exposure to a fixed volume of air overnight, a fixed volume of hydrogen was introduced into the bed. In the case of the unprotected metal, 38 Torr of hydrogen was added and a pressure drop of 10 Torr in 1250 minutes (overall rate of 9.0 x 10^{-7} mol/s/kg) was recorded. For LANA1 SGMH, 53 Torr of hydrogen was added and a pressure drop of 84 Torr in 512 minutes (overall rate of 2.2 x 10^{-5} mol/s/kg) was recorded. Similar rates have been recorded for LANA1 CMH, while somewhat lower rates were observed for ZrCo CMH (see Table 2). The pressure drop recorded in this experiment has been consistently observed when measuring hydrogen absorption from air for composite metal hydrides. The stoichiometric ratio of 1 part air (30 Torr) for 2 parts hydrogen (60 Torr) suggests a recombination or related mechanism, probably removing oxygen gas from the system. When CMH is stored in air without hydrogen present, no similar drop in pressure is observed.

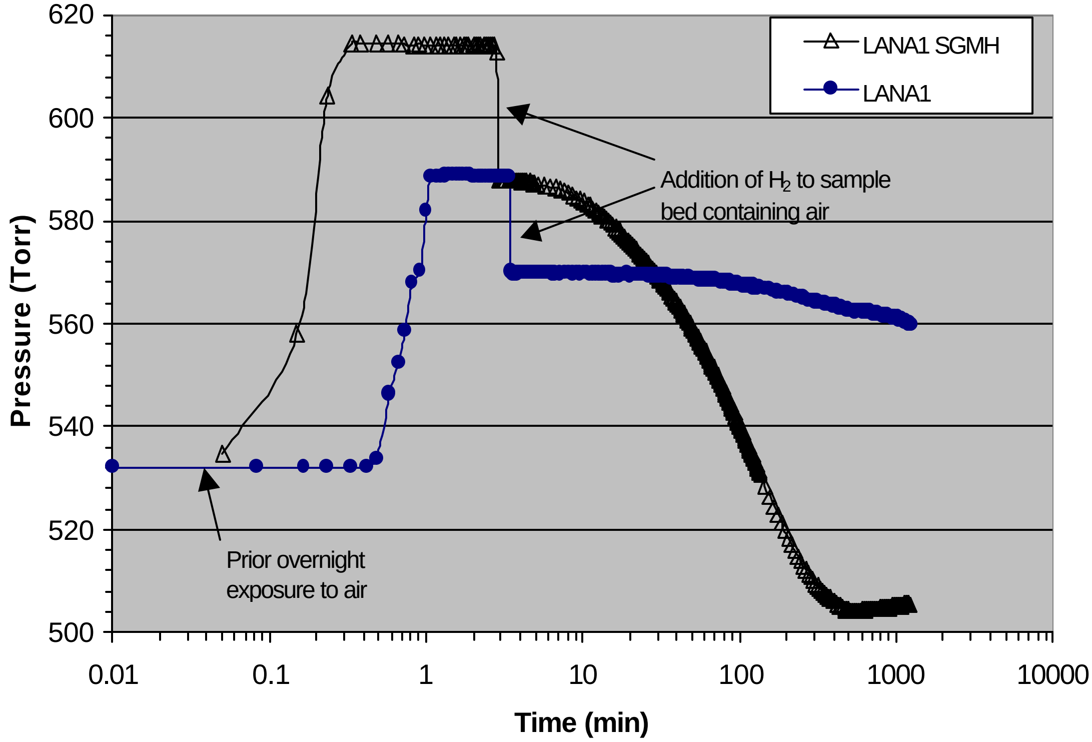


Figure 5. Absorption of hydrogen from air by LANA1 and LANA1 composite.

Figure 6 demonstrates that the potential adsorption or recombination of oxygen in the presence of hydrogen is not detrimental to CMH performance. When 315 Torr of hydrogen was added to a LANA1 SGMH sample in 521 Torr air, the pressure dropped to 412 Torr in 3100 minutes (an overall rate of 1.7 x 10^{-5} mol/s/kg metal). This pressure drop corresponds to the removal of the added hydrogen (315 Torr) plus the oxygen component of the air (109 Torr). Another 80 Torr of hydrogen was then added to same sample in the remaining air and the pressure returned to the initial value of 412 Torr in 850 minutes (overall rate of 1.2 x 10^{-5} mol/s/kg metal). This experiment provides further evidence for the removal of oxygen by composite metal hydrides in the presence of hydrogen. It also demonstrates continued hydrogen absorption by the composite at an acceptable rate once the oxygen is removed. If water is formed from recombination reactions, the moisture absorption capacity of CMH is sufficient to absorb the liquid water.

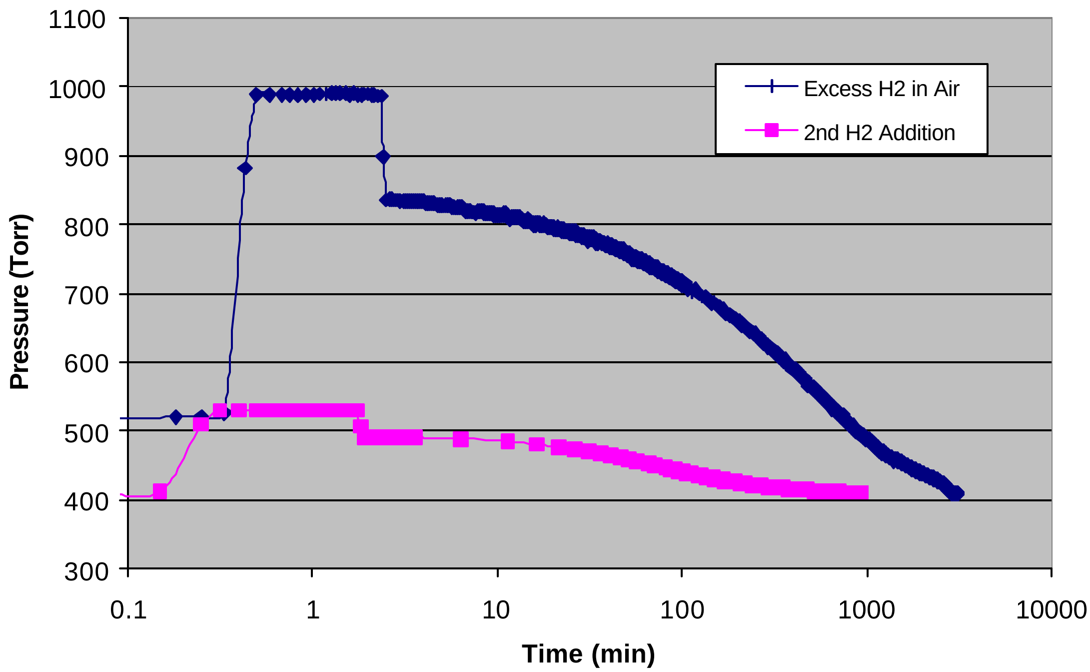


Figure 6. Absorption of a stoichiometric excess of hydrogen in air by LANA1 SGMH.

Example of Sample Results and Data Evaluation

Table 2 summarizes capacity and kinetic data for hydrogen absorption for representative composite metal hydride samples tested to date. The percentage of metal incorporated into composite can be varied somewhat to optimize performance. The total capacities per kilogram of metal measured for small samples were from 70 to 90% of those measured for the metals themselves. The reduced capacity may be caused by inaccessibility of some metal or by non-homogeneous mixing and sampling of the composite materials. Absorption rates in vacuum per kilogram of metal are similar to those for the unprotected metals, and the rates in air are from 10 to 100 times greater than for the unprotected metals. Hydrogen absorption rates in air at 75°C and approximately -20°C for LANA1 SGMH were 5 x 10^{-5} and 3 x 10^{-5} mol/s/kg metal, respectively.

Table 2. Hydrogen Absorption Properties of Some Metal Hydride Composite Getters

Getter	Wt% Metal in Composite	H_2 Capacity (mol/kg comp)	H_2 Capacity (mol/kg metal)	Rate in Vacuum at < 38 Torr H_2 and 25°C (mol/s/kg metal)	Rate in Air at < 5% H_2 and 25°C (mol/s/kg metal)
LANA1 SGMH	35	1.4	4.0	2×10^{-3}	2×10^{-5}
LANA1 CMH	50	2.4	4.8	2×10^{-3}	3×10^{-5}
ZrCo CMH	25	1.7[1]	6.9[1]	Not Measured	5×10^{-6}

[1]Capacity measured at approximately 200ºC during activation step.

Table 3 summarizes CMH getter performance relative to the required hydrogen gettering rates and capacities as prescribed in the SOW. Based on a proposed deployment of getter in the TRUPACT-II ICV, the required hydrogen capacity is 62.2 moles and the minimum required rate is 1.2×10^{-5} mol/s. The observed CMH rates of hydrogen absorption in air are summarized in Table 3. Based on required gettering rates, it is evident that the quantity of composite getter required for the ICV is limited by capacity and not rate. The minimum hydrogen capacity in air is determined by the amount of getter required to maintain the hydrogen concentration below 5% (38 Torr at 1 atm) under normal conditions of transport for the TRUPACT-II.

Table 3. Example of Composite Getter Performance and Required Getter Quantities

Required Rate:	ICV = 1.2×10^{-5} mol/s		Required Capacity:	ICV = 62.2 mol
Getter	H_2 Absorption Rate in Air (mol/s/kg getter)	Minimum H_2 Capacity in Air (mol/kg getter)	Minimum Getter Required (kg)	H_2 Absorption Rate with Required Getter (mol/s)
			ICV	ICV
LANA1 SGMH	7×10^{-6}	0.4	156	1×10^{-3}
LANA1 CMH	1.5×10^{-5}	1.0	63	9×10^{-4}
ZrCo CMH	1.2×10^{-6}	1.7	37	4×10^{-5}

LANA1 composites were found to maintain the hydrogen pressure below 38 Torr at 70°C when loaded to approximately 30 to 35% of the saturation capacity measured at 25°C. Since the saturation capacity reported for ZrCo CMH was measured at 200°C, the minimum capacity at 70°C is expected to be at least 1.7 mol/kg. The getter quantities required (kg) shown in Table 3 are calculated using the required capacity and the minimum hydrogen capacity measured for each CMH getter. The overall absorption rate for each material (mol/s) is calculated from the quantity of getter required (kg) and the hydrogen absorption rate (mol/s/kg). These overall rates are significantly greater than required. The actual hydrogen absorption rate and capacity for CMH will be determined under selected test conditions as part of Phase 1 testing. These values will be used in defining the actual amount of getter required in the TRUPACT-II.

VIII. Points of Contact

This test plan is being executed by a team of scientist and engineers at the Savannah River Technology Center. For additional information on the project, please feel free to contact one of the following individuals:

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